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ENHANCEMENT OR SUPPRESSION OF CIDNP INTENSITIES BY A SECOND MAGNETIC NUCLEUS: INTERPLAY BETWEEN *g* FACTOR DIFFERENCE, EXTERNAL MAGNETIC FIELD, AND HYPERFINE COUPLING CONSTANTS

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The enhancement factors of the ^1H polarization induced in radical pairs generated by α-cleavage of $^{12}C{=}O$- and $C{=}O$-labelled ketones deviate from the ratios expected on the basis of the relative abundances of the respective carbon isotopomers. For dibenzyl ketone, the ratio of absolute CIDNP intensities of the $^1H(^{13}C)$ doublet (90% $^{13}C{=}O$) to the $^1H(^{12}C)$ singlet (10% $^{12}C{=}O$) was found to be >9:1 at 58·3 kG and <9:1 at 21 kG. Similar deviations were observed for other ^{13}C labelled ketones, viz. deoxybenzoin ($^{13}C{=}O$) and acetophenone ($^{13}C{=}O$ or $^{13}CH_3$). This novel enhancement or suppression effect on the CIDNP enhancement can be ascribed to the presence of a second hyperfine coupled nucleus in the intermediate radical pair. The individual contributions of the g factor difference (Δg), **the external magnetic field strength (H_0), and the hfc constants of the observed (a_A) and the interacting nucleus (a_X) in the enhancement–suppression are exemplified. The experimental results are consistent with theoretical calculations of the mutual effect of Δg, H_0, a_A and a_X on the CIDNP enhancement factor of the observed nucleus.**

INTRODUCTION

Since its discovery[1] in 1967, the phenomenon of chemically induced dynamic nuclear polarization (CIDNP) has been intensively studied.[2,3] It has been amply demonstrated that this technique is a very powerful tool for investigating organic reaction mechanisms.[3,4] In 1971, Kaptein[5] formulated two simple qualitative sign rules to account for the polarization phases of nuclei, and these rules have been widely used to assign the magnetic parameters of the intermediate radical (ion) pairs. Most reported CIDNP studies were focused on the polarization of a single type of nucleus, typically ^1H. Only a limited number of studies exist that probe the effect of a second magnetic nucleus with an appreciable hyperfine coupling constant (hfc) on the CIDNP pattern and enhancement factor of the 'primary' nucleus.

Several years ago, Roth and co-workers[6a,b] and others[6c,d] drew attention to the CIDNP patterns in systems containing a second nucleus with a sizable hfc constant. The CIDNP spectra of such systems often deviate from those predicted by Kaptein's rules. We also observed that the CIDNP enhancement factor of nuclei could be suppressed by the presence of a second nucleus.[7] More pronounced suppression effects could be observed if the second nucleus has a larger hfc constant than the nucleus under consideration. In this paper we report a novel phenomenon: CIDNP intensities can be either reduced or enhanced owing to interaction with a second magnetic nucleus. The degree of enhancement or suppression depends on the external magnetic field strength (H_0), the electron g factor difference (Δg) and the ratio of the hfc constants. The observed phenomena can be reproduced accurately by the 'exact radical pair' theory of CIDNP.

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EXPERIMENTAL

Solutions of 10–20 mM ketones in acetonitrile (Aldrich, 99% D) or cyclohexane-d_6 (Aldrich, 99% D) were purged with argon for 5–10 min and irradiated in an NMR probe as described elsewhere.[6b,7] The CIDNP experiments at 58.3 kG were performed on a Bruker 250 MHz AF Fourier transform (FT) NMR spectrometer. The collimated beam of a Hanovia 1000 W high-pressure mercury lamp was filtered through aqueous $CoSO_4$ solution and guided via a fused-silica rod, with mirrors at both ends, into a modified NMR probe. The experiment at 21 kG was executed on a Bruker WH 90 FT NMR *spectrometer with* a 200 W Hanovia high-pressure mercury lamp as light source. In all experiments, a pulse angle of 15–25° was used to minimize distortion of the multiplet intensities. The number of scans was adjusted to obtain a satisfactory signal-to-noise ratio. During the irradiation dibenzyl ketone and deoxybenzoin were noticeably depleted (5–20%). However, with acetophenone, the consumption of the starting ketone is negligible, since the starting ketone is regenerated from the intermediate radical pair. All CIDNP spectra were obtained by subtraction of a dark spectrum, recorded either immediately before or after photolysis, from the spectrum recorded during irradiation.

The materials used were dibenzyl ketone (DBK) (90% $^{13}C{=}O$) and deoxybenzoin (90% $^{13}C{=}O$), synthesized according to literature procedures,[6b] and acetophenones labelled in the carbonyl (90% $^{13}C{=}O$) or methyl position (91·3% $^{13}CH_3$), purchased from MSD isotopes and Prochem (London, UK), respectively.

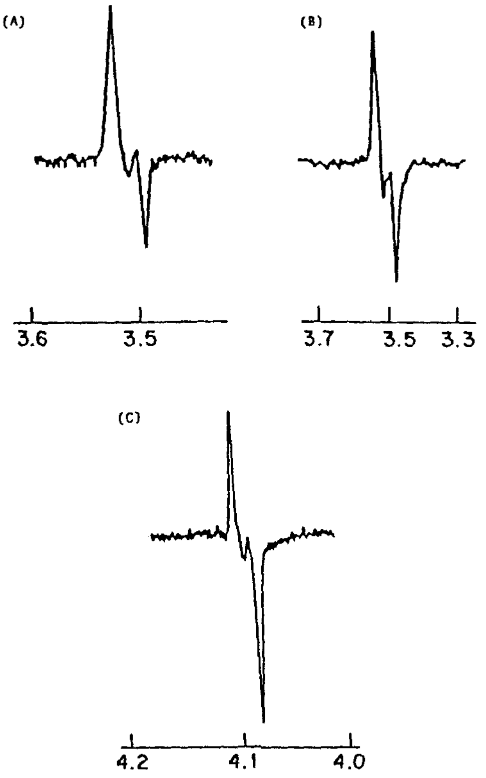

Figure 1. ^1H CIDNP of the benzylic protons of 20 mM dibenzyl ketone (90% $^{13}C{=}O$) in acetonitrile-d_3 at an external magnetic field of (A) 58·3 kG or (B) 21 kG, and (C) of 20 mM deoxybenzoin (90% $^{13}C{=}O$) in acetonitrile-d_3 at a field of 58·3 kG

RESULTS

Photolysis of dibenzyl ketone[8] results in α-cleavage, generating a radical pair, benzyl–phenylacetyl, initially of triplet spin multiplicity. Following intersystem crossing (isc) to the singlet state, this pair may recombine to regenerate the starting material. As a result of the radical pair interaction the benzylic protons show emissive nuclear polarization[9] at all fields at which the reaction was studied (14, 21 and 58.3 kG). When the carbonyl carbon is ^{13}C labelled, the NMR signal of the benzyl protons is split into a doublet and an A/E polarization pattern (enhanced absorption for the low-field signal, emission for the high-field signal) is observed [Figures 1(A) and (B)]. We had noted previously[6] that the multiplet shows net absorption at both 21 and 58·3 kG, contrary to the polarization direction predicted by Kaptein's net rule.[5] Since the DBK used in this study contained 90% $^{13}C{=}O$, one might have expected that the ratio of the polarization intensities for the outer doublet and the central singlet (associated with 10% $^{12}C{=}O$) would reflect the ratio of isotopomers, 9:1. However, the observed ratio is larger (11:1) at 58·3 kG [Figure 1(A)] and smaller (8·2:1) at 21 kG [Figure 1(B)]. A comparison of Figures 1(A) and (B) clearly shows the effect of the external magnetic field strength on the CIDNP enhancement factor.

Similar effects are observed for the benzyl protons of 90% $^{13}C{=}O$-labelled deoxybenzoin at 58·3 kG [Figure 1(C)]. Once again, at high magnetic field (58·3 kG) *the intensity ratio of the outer doublet to the* central singlet is larger (12:1) than expected on the basis of the 9:1 isotopic abundance. The deviation in the polarization intensities ratio is clearly due to the external magnetic field and the second magnetic nucleus. By the presence of the ^{13}C carbonyl ($^{13}C{=}O$), the CIDNP intensities (or enhancement factor) of the benzyl protons are enhanced at 58·3 kG and suppressed at 21 kG.

In order to evaluate the effect of Δg on the CIDNP enhancement factor, acetophenone (90% $^{13}C{=}O$) was irradiated at 58·3 kG in the presence of different hydrogen donors, viz. phenol[10] and diphenylamine. Photoexcited acetophenone reacts with either substrate by hydrogen abstraction, generating α-phenylhydroxymethyl radicals paired with either a phenoxyl or an *N*,*N*-diphenylaminyl radical [equation (1)]. These radical pairs, initially of triplet multiplicity, can either undergo intersystem crossing [equation (2)] or diffuse apart ('escape') to generate free radicals [equation (4)]. Intersystem crossing can be followed by reverse hydrogen transfer ('disproportionation'), either regenerating the ketone or generating an enol [equations (3a) and (3b)]. Enol-to-ketone tautomerization also regenerates acetophenone [equation (5)]. As a result of this reaction sequence, the methylene protons of the enol and the methyl protons of the regenerated acetophenone are overpopulated in the β nuclear state (emissive nuclear polarization).

$$\mathrm{PhCOCH_3 + DH} \xrightarrow{h\nu} {}^3[\mathrm{Ph\dot{C}(OH)CH_3}\ \cdot\mathrm{D}] \tag{1}$$

where D = PhO or $(\mathrm{Ph})_2\mathrm{N}$);

$${}^3[\mathrm{Ph\dot{C}(OH)CH_3}\ \cdot\mathrm{D}] \xrightarrow{\mathrm{isc}} {}^1[\mathrm{Ph\dot{C}(OH)CH_3}\ \cdot\mathrm{D}]$$

$$[\mathrm{PH\dot{C}(OH)CH_3}\ \cdot\mathrm{D}] \rightarrow \mathrm{DH}\ddagger + \mathrm{PhC(OH){=}CH_2}\ddagger \tag{3a}$$

where ‡ represents a polarized nucleus;

$$[\mathrm{Ph\dot{C}(OH)CH_3}\ \cdot\mathrm{D}] \rightarrow \mathrm{DH}\ddagger + \mathrm{PhCOCH_3}\ddagger \tag{3b}$$

$${}^3[\mathrm{Ph\dot{C}(OH)CH_3}\ \cdot\mathrm{D}] \rightarrow \mathrm{Ph\dot{C}(OH)CH_3} + \cdot\mathrm{D} \tag{4}$$

$$\mathrm{PhC(OH) = CH_2}\ddagger \rightarrow \mathrm{PhCOCH_3}\ddagger \tag{5}$$

We have studied these reactions with acetophenone labelled in either the carbonyl or methyl position. The polarization patterns observed for the CH_3 signal of $[^{13}C{=}O]$acetophenone during the photoreaction with diphenylamine and phenol as hydrogen donor, respectively, are shown in Figures 2(A) and (B). Once again, the outer doublets represent the methyl protons coupled to $^{13}C{=}O$ (90% ^{13}C), whereas the central peaks are due to methyl groups adjacent to $^{12}C{=}O$ (10% ^{12}C). The ratio of the doublet intensity (i.e. the sum of absolute intensities) to the singlet intensity is >30:1 for the reaction with diphenylamine [Figure 2(A)] and 9·2:1 for the reaction with phenol [Figure 2(B)].

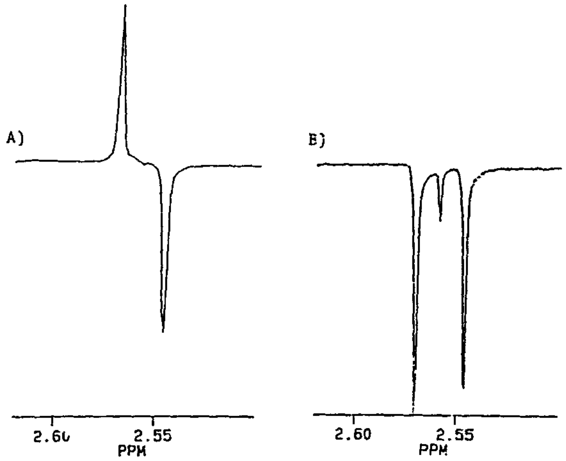

Figure 2. ^1H CIDNP of the methyl protons of 10 mM acetophenone (90% $^{13}C{=}O$) in acetonitrile-d_3 in the presence of (A) 20 mM diphenylamine or (B) 20 mM phenol at a field of 58·3 kG

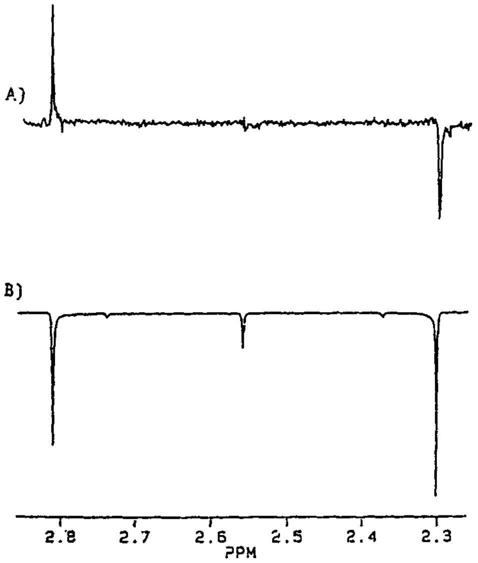

Figure 3. ^1H CIDNP of the methyl protons of 10 mM acetophenone (91·3% $^{13}CH_3$) in acetonitrile-d_3 in the presence of (A) 20 mM diphenylamine or (B) 20 mM phenol at a field of 58·3 kG

With $^{13}CH_3$-labelled acetopheone (91·3% $^{13}CH_3$), the magnitude of the second hfc changes from 6·68 G[11] (of ^{13}COH) to 5·5 G[11] (of $^{13}CH_3$), which causes slightly different CIDNP patterns for the methyl protons of the regenerated acetophenone [Figures 3(A) and (B) with diphenylamine and phenol as hydrogen donor, respectively). The data in Figures 2(A) and 3(A) are remarkable, since they show pronounced multiplet effects with the polarization of the central singlet near zero. The CIDNP intensity ratio of doublet (coupled to $^{13}CH_3$) to singlet (attached to $^{12}CH_3$) in the reaction with phenol is 9:1, smaller than the ratio of $^{13}C(H_3)$ to $^{12}C(H_3)$ in the reagent acetophenone.

DISCUSSION

Under the influence of an external magnetic field, the electron spin will precess along the axis of the field at a frequency, ω, as defined by the equations[2b]

$$\omega_{s1} = \beta\hbar^{-1}(g_1H_0 + \Sigma a_1m_1) \tag{6a}$$

$$\omega_{s2} = \beta\hbar^{-1}(g_2H_0 + \Sigma a_2m_2) \tag{6b}$$

where g_i is the electron g factor, a_i is the electron–nuclear hfc constant and m_i is the nuclear spin quantum number. The difference in the precession frequencies of the two electrons of a given radical pair can be expressed by

$$\begin{aligned}\Delta\omega &= (\omega_{s1} - \omega_{s2})\\ &= \beta\hbar^{-1}[(g_1 - g_2)H_0 + (\Sigma a_1m_1 - \Sigma a_2m_2)]\end{aligned} \tag{7}$$

Accordingly, the overall intersystem crossing rate is determined by two independent terms, the ΔgH_0 and hyperfine terms. In the absence of a magnetic nucleus, the electron spin of each radical precesses around the external magnetic field axis with a constant rate proportional to ΔgH_0. In the presence of a magnetic nucleus, the electron–nuclear interactions cause the electron energy to be split into two different levels; accordingly, the electron spins will precess at two different frequencies, each associated with, and determined by, a nuclear spin state. The CIDNP intensity is determined by the square roots of the two electron precession frequencies:

$$I \propto [(\Delta\omega_1)^{1/2} - (\Delta\omega_2)^{1/2}] \tag{8}$$

Figure 4 shows the theoretical calculation of CIDNP intensities for the DBK system as a function of the parameter G:

$$G = \Delta gH_0/a_A \tag{9}$$

where a_A is the hfc of the nucleus under consideration;[6a] this approach is an extension of a method developed by Closs[12a] and Müller.[12b] In Figure 4, curves 1 and 2 represent the intensities of the benzylic doublet coupled to the carbonyl $^{13}C(=O)$, whereas curve 3 is the summation of the absolute intensities of curves 1 and 2. Curve 4 is the calculated net intensity of benzylic protons adjacent to $^{12}C(=O)$. The benzyl radical has an electron g factor of 2·0026 and a benzylic ^1H hfc of −16·3 G; the phenylacetyl radical has an electron g factor of 2·0008 and the carbonyl carbon has an hfc of 130 G.[13] The magnetic parameters for the radical pair generated from the deoxybenzoin system are identical or very close to those of the DBK system. One of the doublets (Figure 4, curve 2) is strongly field dependent. As pointed out before,[6a] the cross-over point G_{cr}, where curve 2 has zero CIDNP intensity, depends strongly on the second hfc (a_X). The theoretical calculation predicts that the CIDNP enhancement will depend on Δg, H_0 and the ratio a_X:a_A. Compared with the polarization in the absence of a second nucleus (curve 4), the enhancement factor of the benzylic protons would be reduced by the presence of the carbonyl $^{13}C(=O)$ at 21 kG and increased at 58·3 kG, in full agreement with the observed results (Figure 1).

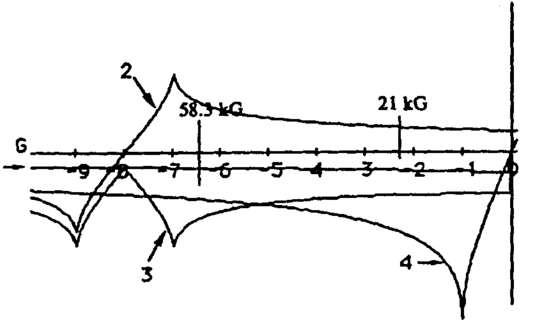

Figure 4. Calculated CIDNP intensities for a two-spin system of $a_A = -16·3$ G, $a_X = 130$ G, $g_1 = 2·0026$ and $g_2 = 2·0008$. Curves 1 and 2 represent the intensities of the individual doublet lines of nucleus A; curve 3 is the sum of the absolute intensities of the doublet signals (curves 1 and 2); curve 4 is the polarization intensity of the nucleus A in the absence of nucleus X

In the case of acetophenone, hydrogen abstraction by the excited carbonyl group from various donors generates the α-phenylhydroxymethyl radical with an electron g factor of 2·00302,[11,13a] a methyl ^1H hfc of +14.1 G[13a] and a $^{13}C(—C—O^-)$ hfc of +6·68 G.[11] The CIDNP pattern of the methyl protons depends strongly on the electron g factor of the geminate counter radical. Diphenylaminyl radical has an electron g factor of 2·0032,[14] whereas for the phenoxyl radical $g = 2·0051$.[15] In the case of the α-phenylhydroxymethyl–diphenylaminyl radical pair, the Δg is very small (*ca* 0·00018). Even at a field as high as 58·3 kG, the multiplet effect is very pronounced and dominates the observed effect (see Figure 2 for experiment, curves 1 and 2 of Figure 5 for theoretical prediction). The near-zero polarization of the methyl signal associated with $^{12}C{=}O$ (i.e. the central singlet) strongly suggests that the g values of α-phenylhydroxymethyl and diphenylaminyl radicals are almost identical. Therefore, the system shows a nearly 'pure' multiplet effect (cf. the value $G \approx 0$ in Figure 5).

The radical pair generated by the photoreaction of acetophenone with phenol has a relatively large Δg value, *ca* 0·0021 ($g_{C\cdot OH} = 2·00302$,[11,13a] $g_{ArO\cdot} = 2·0051$[15]). In this case, the net effect (ΔgH_0 term) dominates the multiplet effect (the hyperfine term). The magnitude of the magnetic parameters corresponds to a value $G = -8·6$ (Figure 6). The methyl doublet of acetophenone ($^{13}C{=}O$) shows net emissive polarization. The intensity summation of the doublet is essentially equal to that of the methyl protons of acetophenone ($^{12}C{=}O$). The experimentally observed ratio

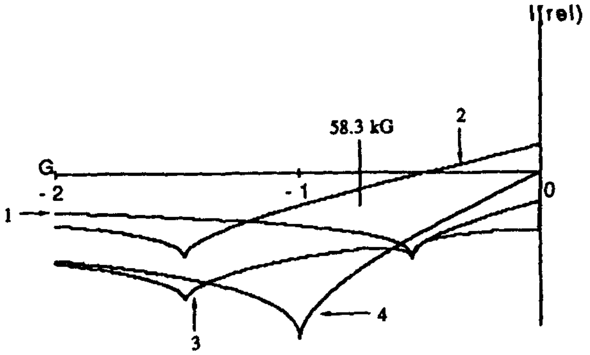

Figure 5. Calculated CIDNP intensities for a system of $a_A = 14{\cdot}1$ G, $a_X = 6{\cdot}68$ G, $g_1 = 2{\cdot}00302$ and $g_2 = 2{\cdot}0032$. Curves 1 and 2 represent, respectively, the low- and high-field signals of nucleus A; curve 3 is the sum of the absolute intensities of the doublet signals; curve 4 is the polarization intensity of the nucleus A in the absence of nucleus X

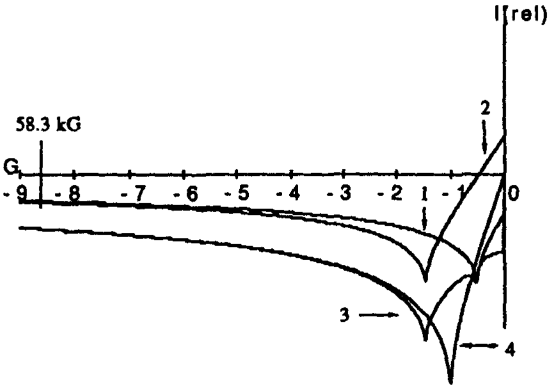

Figure 6. Calculated CIDNP intensities for a two-spin system of $a_A = 14{\cdot}1$ G, $a_X = 6{\cdot}68$ G, $g_1 = 2{\cdot}00302$ and $g_2 = 2{\cdot}0051$. Curves 1 and 2 represent the signals of nucleus A; curve 3 is the sum of the absolute intensities of the doublet; curve 4 is the polarization intensity of the nucleus A in the absence of nucleus X

fits the theoretically predicted one value fairly well. This particular example shows an 'unexceptional' effect of the second nucleus on the CIDNP enhancement factor of the observed nucleus.

Changing the acetophenone ^{13}C label from the carbonyl to methyl position slightly reduces the magnitude of the second hfc. This is not expected to affect the polarization induced in the α-phenylhydroxymethyl–phenoxyl radical pair, since the $\Delta g H_0$ term strongly dominates the hyperfine term. Indeed, the CIDNP patterns of Figures 2(B) and 3(B) are very similar; the intensity ratios of the ^{13}C–H doublet to the ^{12}C–H singlet are close to the respective isotopomer ratio. For the α-phenylhydroxymethyl–diphenylaminyl radical pair, on the other hand, reducing the magnitude of the second hfc does not change the CIDNP patterns [see Figures 2(A) and 3(A)]. This can be ascribed to a much smaller contribution to the $\Delta g H_0$ term (i.e. $\Delta g H_0 \approx 0$) to the overall intersystem crossing of the intermediate radical pair.

The experimental and calculated CIDNP intensity ratios of the systems studied are summerized in Table 1. Most of the experimentally observed CIDNP intensity ratios are in acceptable agreement with those calculated, with the notable exceptions of the results observed during the photolysis of DBK at 21 kG. The reason for this discrepancy is not obvious, insufficient resolution being one possible explanation. The noticeable overlap of the ^{12}C with the lower field ^{13}C signal may distort the assigned ratio. This effect may be amplified by the subtraction yielding the CIDNP spectra.*

The above examples demonstrate that Δg, H_0 and the magnitude of the second hfc all affect the CIDNP enhancement of the nucleus under study. The interdependence of the individual parameters is illustrated by Figure 7, where the relative CIDNP intensities of nucleus A (z axis) are plotted as a function of a_X (x axis) and the parameter G (y axis). Figure 7(a) and (b) show the CIDNP intensities of the doublet, whereas Figure 7(c) and (d) show the sum of the doublet intensities and the sum of the absolute intensities, respectively.

One of the signals [Figure 7(a)] always has the polarization predicted by Kaptein's net effect rule.[5] The magnetic field strength, $H_{0,\max}$, at which this signal reaches maximum intensity decreases with increasing

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*A referee raised the question of how changes in radical pair lifetimes (due to a chemical process, e.g. decarbonylation) affect the CIDNP enhancement factor and whether the large discrepancy between the observed and calculated CIDNP ratios for DBK could be ascribed to a breakdown of equation (8). Our previous study[16] has shown that the most efficient spin sorting is achieved when the competing process(es) (e.g. diffusional separation, decarbonylation or chemical transformation reactions) are compatible with the intersystem crossing rate of radical pairs. A mismatch between the competing rates leads to less efficient spin sorting and, therefore, smaller CIDNP enhancement. For a given intersystem crossing rate, a change of radical pair lifetime (due to decarbonylation) will change the absolute CIDNP enhancement. Similarly, for a given competing process, the variation of the intersystem crossing of radical pairs, due to the incorporation of additional magnetic nuclei (α and β), will change the absolute CIDNP enhancement. In the case of DBK, the competing chemical process is the same for all radical pairs, regardless of the presence of a ^{13}C nucleus and, therefore, does not show any net effect on the relative CIDNP enhancement factor. We are not aware of any conditions which cause a breakdown of equation (8).

Table 1. Experimentally observed and theoretically calculated CIDNP intensity ratios of ^{13}CH (outer doublet) to ^{12}CH (central singlet) of systems containing a second magnetic nucleus

	Observed		Interacting		ΔgH_0	CIDNP ratio	
Product	Nucleus	hfc (G)	Nucleus	hfc (G)	(G at 58·3 kG)	Observed	Calculated
DBK[a]	Benzylic H	−16·3	90% ^{13}C=O	130	104·9	11:1	12·8:1
					37·8[b]	8:1	4·9:1
DB[a]	Benzylic H	−16·3	90% ^{13}C=O	130	104·9	12:1	12·8:1
AP[a]	Methyl H	+14·1	90% ^{13}C=O	6·68	10·5[c]	>30:1	>30:1
					121·3[d]	9:1	9·0:1
			91·3% ^{13}CH$_3$	5·5	10·5[c]	>30:1	>30:1
					121·3[d]	9:1	10·5:1

[a] DBK, dibenzyl ketone; DB, deoxybenzoin; AP, acetophenone.
[b] At a field $H_0 = 21$ kG.
[c] The proton donor is diphenylamine.
[d] The proton donor is phenol.

values of a_X, and reaches zero field (H_0,max = 0) when $a_X = a_A$. The direction of the second signal [Figure 7(b)] depends on Δg, H_0 and a_X; its value of $H_{0,\max}$ increases with a_X. At low fields the two signals of the doublet always have opposite directions; their intensities reach maximum values when $a_X = a_A$. The net polarization (viz. the sum of the individual intensities) of the doublet [Figure 7(c)] becomes opposite to that predicted by Kaptein's net effect rule at low magnetic fields. The 'anti-Kaptein' effects are observed for values of $a_X > a_A$; they cover a broad region for large ratios of a_X:a_A and vanish at $a_X = a_A$. The existence of this region has been experimentally documented.[6a,b]

Figure 7(d) shows the sum of the absolute intensities of the two doublet signals. For any value of a_X (i.e. in any I_{CIDNP} vs G plane) there exist two maxima and one minimum. The two maxima occur at magnetic fields where the contributions of the g factor and the hyperfine terms to the precession frequency of a given electron spin cancel each other [equation (6)]. The magnetic field, $H_{0,\max}$, can be defined as

$$H_{0,\max} = |(a_A \pm a_X)/\Delta g| \tag{10}$$

Hence the larger the second hfc, the farther apart the two maxima grow.

The CIDNP enhancement factor reaches a local maximum when the CIDNP intensities of the doublet signals reach a local maximum. The G ($= \Delta g H_0/a_A$) values at the two local maxima can be expressed as a function of a_A and a_X, i.e.

$$G_{\max} = \mathrm{sign}(\Delta g)\,|1 \pm a_X/a_A| \tag{11}$$

Substitution of equation (10) into equations (7) and (8) yields the CIDNP intensities at the two local maxima as a smooth and continuous function of a_X. Therefore, the 'rugged' appearance of the CIDNP intensity along the two local maxima (Fig. 7) is an artifact of the low graphic resolution of the Macintosh computer used. Between the two local maxima, there exists a local minimum the position of which can be derived from equations (10) and (11). When $|a_A| \geqslant |a_X|$, the field strength of the local minimum is

$$H_{\min} = |a_A/\Delta g| \tag{12a}$$

i.e. the field at the valley point is independent of the magnitude of the second hfc. When $|a_A| \leqslant |a_X|$, the field strength at the local minimum becomes

$$H_{\min} = |a_X/\Delta g| \tag{12b}$$

The field strength of the second local minimum increases with increasing values of a_X, coincides with the first local minimum [equation 12(a)] at the point $a_X = a_A$, and becomes the dominant minimum for values $a_X > a_A$ [equation 12(b)]. Near this minimum, the CIDNP enhancement factor of the doublet is always smaller than that of the central singlet. In other words, there exists a region where the enhancement factor of the observed nucleus can be 'suppressed' by the presence of a second hfc; the larger is the magnitude of the second hfc, the larger are the degree of 'suppression' and its range. A small hfc can also cause a suppression effect on the CIDNP enhancement factor of an observed nucleus with a larger hfc, although the suppression region is relatively smaller (see Fig. 7); this has been observed previously.[7]

Curve 1 on the front of Fig. 7 describes the field-dependent behavior of the CIDNP intensity in the absence of a second hfc. The maximum net CIDNP effect occurs at a field ($H_{0,\max,\mathrm{net}}$) of

$$H_{0,\max,\mathrm{net}} = |a_A/\Delta g| \tag{13}$$

where one of the electron precession frequencies of the intermediate radicals is zero. This curve also describes the generally observed tendency that the CIDNP intensity originated from a radical pair with a large Δg or a small a_A, decreases towards relatively high fields. For example, a radical pair with a Δg of 0.0017 and a_A of −16 G (e.g. the phenylacetyl–benzyl radical pair from

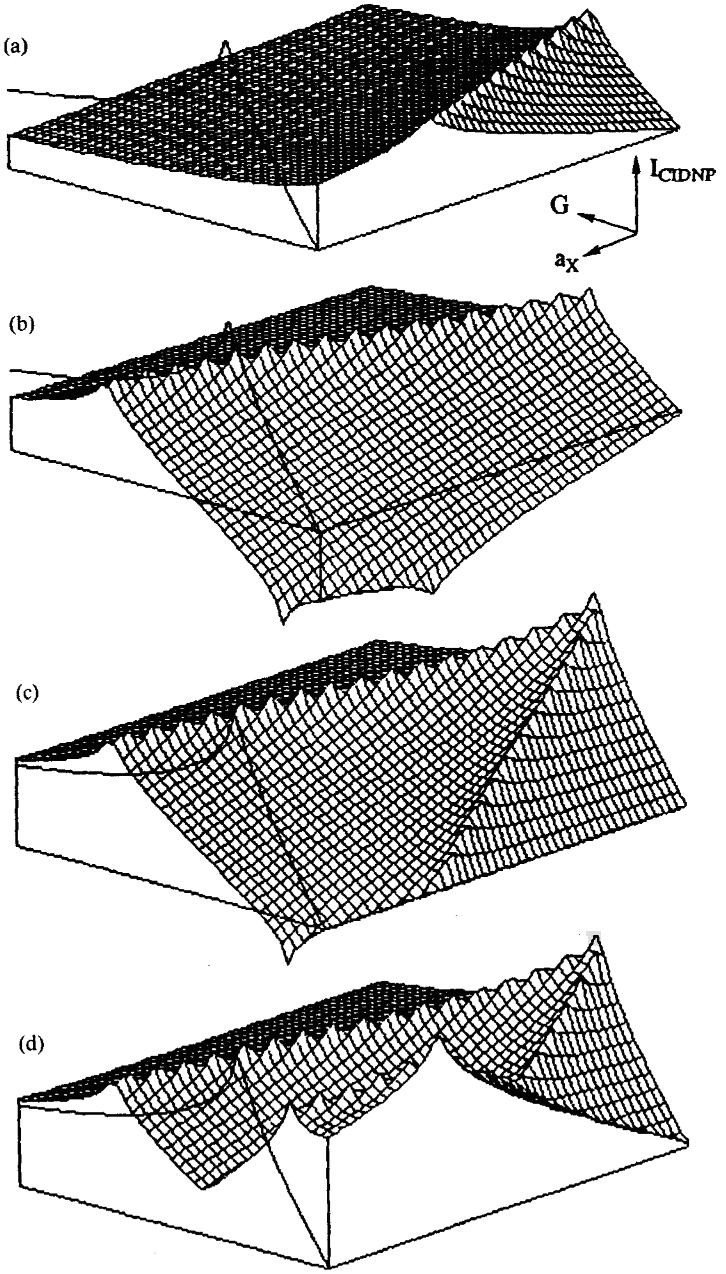

Figure 7. Computer simulation of relative CIDNP intensities (I) for a doublet of a nucleus A as a function of the hfc of a second nucleus X (a_X) and of the parameter G ($=\Delta g H_0/a_A$). The graph contains I vs G plots for values of $0 < a_X < 70$ G at increments of 1·4 G. For ease of comparison, curve 1 for $a_X = 0$ G is plotted also at the value $a_X = 70$ G. The parameters used in the simulation are $a_A = 50$ G, $\Delta g = 0{\cdot}0016$ and $G = 0$ to $-3{\cdot}5$. (a) and (b) show the intensities of the individual signals; (c) shows the sum of (a) and (b); (d) shows the sum of the absolute intensities of (a) and (b)

photolysis of dibenzyl ketone) will have a maximum CIDNP at a field of 9·4 kG, equivalent to a ^{1}H frequency of 40 MHz. At high magnetic fields, viz. 58·3 kG (*ca* 250 MHz for ^{1}H), the CIDNP intensity observed from such a radical pair will be relatively small.

Pronounced suppression occurs at fields where the central singlet has maximum intensity (i.e. $H_0 = |a_A/\Delta g|$), or when the doublet has minimum intensity [i.e. at a field of $|a_A/\Delta g|$ and/or $|a_X/\Delta g|$; cf., equations (12)]. When the two coupled nuclei have similar hfc constants (i.e. $|a_A| \approx |a_X|$), the fields where the central singlet and the outer doublet reach a maximum and minimum, respectively, are close to each other, as illustrated in Figures 5 and 6, respectively. In other words, the most pronounced suppression is predicted for a system with $|a_A| \approx |a_X|$ at a field $H_0 = |a_A/\Delta g|$. When the hfc of the second nucleus is much larger than that of the observed nucleus ($|a_X| \gg |a_A|$), there exist two pronounced suppression regions, as shown in Figure 4.

The rightmost surface of Figure 7(d) represents the CIDNP intensity as a function of the magnitude of the second hfc (a_X). At zero field or for a system with $\Delta g = 0$, only the multiplet effect can be observed. Figure 7(d) shows that the multiplet effect for systems with $\Delta g = 0$ or at zero field (the $I_{\rm CIDNP}$ vs a_X plane at $G = 0$) increases monotonically as a function of the second hfc (a_X), and reaches a maximum when $|a_X| = |a_A|$ [equation (11)], where two of the four electron precession frequencies associated with the corresponding radical pair are zero. At this particular point $|a_X| = |a_A|$, increasing the G value (i.e. increasing the external field strength for systems with $\Delta g \neq 0$, or increasing the Δg value of a system at a non-zero field) causes the absolute intensities of the individual signals (and the enhancement factor) to fall off sharply. The signal intensities reach a minimum at a field of $H_{0,\rm min} = |a_X/\Delta g|$ [equation (12b)], and then increases to a second maximum at a field of $H_{0,\rm max} = (|a_X| + |a_A|)/|\Delta g|$.

CONCLUSION

We have observed novel enhancement–suppression effects on the CIDNP intensities of several ^{13}C-labelled ketones, namely dibenzyl ketone (90% ^{13}C=O), deoxybenzoin (90% ^{13}C=O) and acetophenone (either 90% ^{13}C=O or 91·3% ^{13}CH$_3$). These novel effects are due to the presence of a second hfc, and are dependent on the difference in the electron g factors (Δg), the external magnetic field strength (H_0) and the hfc constants of the observed and the coupling nuclei. Theoretical calculation shows that there exist two maximum enhancement regions at fields of $|(a_X \pm a_A)/\Delta g|$, respectively. The most pronounced suppression effect occurs at fields $H_0 = |a_X/\Delta g|$ and $H_0 = |a_A/\Delta g|$ regions (for a system with $|a_X| = |a_A|$, the most pronounced suppression occurs at a field $H_0 = |a_A/\Delta g|$). At an appropriate field, a small hfc can also cause a suppression effect on the CIDNP enhancement factor of a nucleus with a larger hfc.[7] The radical pair theory also predicts that the pure multiplet effect for systems with $\Delta g = 0$ (or systems with $\Delta g \neq 0$ at $H_0 = 0$) reaches a maximum when the hfc constants of the observed and the coupling nuclei are equal.

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